TOXIC MONITORING IN THE SUSQUEHANNA RIVER AT MARIETTA, PENNSYLVANIA

SUSQUEHANNA RIVER BASIN COMMISSION

NOVEMBER 1992

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* Statutory Citations: Federal - Pub. L. 91-575, 84 Stat. 1509 (December, 1970); Maryland - Natural Resources Sec. 8-301 (Michie 1974); New York - ECL Sec. 21-1301 (McKinney 1973); and Pennsylvania - 32 P.S. 820.1 (Supp. 1976).

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AT MARIETTA, PENNSYLVANIA

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SUSQUEHANNA RIVER BASIN COMMISSION
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Publication No. 147

November 1992

CONTENTS

ILLUSTRATIONS

TABLES

ABSTRACT

There has been an increased concern that the ecosystems of the Chesapeake Bay are being affected by toxic chemicals. Little work has been done to identify toxic substances entering the Bay from the Susquehanna River; therefore, sampling for toxic substances was added to the existing the Susquehanna River Basin Commission nutrient monitoring program.

The objectives of the study were to characterize at Marietta, Pa., (Hydrologic unit 0156000) the concentrations of selected trace metals and pesticides during base flow and stormflow and to provide data needed to design future toxics monitoring programs.

Rainfall deficiencies at the beginning of the sampling effort brought on drought conditions for most of the study period and prevented collection of data needed for definitive evaluation of seasonal variability and variability between low flow and stormflow.

Copper, lead, nickel, zinc, and aluminum were the most prevalent metals transported by the Susquehanna River at Marietta, Pa. Copper, lead, nickel, and zinc concentrations are storm related and increase with increasing flow. Mercury, silver, cadmium, and chromium were detected mostly in concentrations less than the laboratory reporting value. Chromium concentrations appear to be storm related. Arsenic was detected only in storm samples.

Atrazine, propazine, and lindane were the only pesticides detected and in concentrations which were less than the laboratory reporting value. Pesticides were not detected in the single storm which occurred in March 1992,

possibly because runoff occurred nearly a year after pesticide application and prior to new pesticide application.

INTRODUCTION

The Pennsylvania Department of Environmental Resources (Pa. DER), Bureau of Land and Water Conservation and Bureau of Laboratories, the U.S. Environmental Protection Agency (U.S. EPA), and the Susquehanna River Basin Commission (SRBC) cooperated in a one-year study to collect trace metal and selected pesticide data.

Background

There has been increased concern among the participants in the Chesapeake Bay Program that the ecosystems of the Chesapeake Bay are being affected by toxic chemicals. There has been little work done to identify toxic substances entering the Bay from the Susquehanna River. Therefore, sampling for toxic substances was added to the existing SRBC nutrient and suspended-sediment monitoring program to enhance our understanding of the transport of selected toxic constituents. The objective of the sampling effort necessitated collection of samples during high-flow events, as well as base flow, since a substantial portion of the load is contributed during high-flow events.

Purpose and scope

This one-year sampling effort was to serve as a pilot study to learn how best to design an informative and affordable long-term monitoring program. The objectives of the study were to:

1. Characterize at Marietta (hydrologic unit 01576000) the concentration of selected metals and pesticides during base flow and stormflow.
2. Provide information needed to refine future toxics monitoring programs for the Chesapeake Bay Program.

This report presents the data collected during the period May 1991 to April 1992.

DESCRIPTION OF THE SUSQUEHANNA RIVER BASIN

The Susquehanna River (fig. 1) drains an area of 27,510 square miles (Susquehanna River Basin Study Coordination Committee, 1970) and is the largest tributary to the Chesapeake Bay.

The climate in the Susquehanna River basin varies considerably from the low lands adjacent to the Chesapeake Bay in Maryland to the high elevations, above 2,000 feet, of the northern headwaters in central New York state. The annual mean temperature ranges from 53°F (degrees Fahrenheit) near the Pennsylvania/Maryland border to 45°F in the northern part of the basin. Precipitation in the basin averages 39.15 inches per year and is fairly well distributed throughout the year.

The average growing season in the southern part of the basin is approximately 160 days and lasts from about May 1 to about October 10. The growing season in the northern part of the basin is roughly 120 days and extends from about May 15 to September 15. However, frost can occur significantly later in the spring and earlier in the fall than the beginning and ending dates of the average growing season.

Land use in the Susquehanna River basin above Marietta is predominantly rural. Woodland accounts for 65 percent of land use; grassland, 7 percent; cultivated, 18 percent; and urban, 9 percent (Ott and others, 1991). Woodland occupies the higher elevations of the northern and western basin and much of

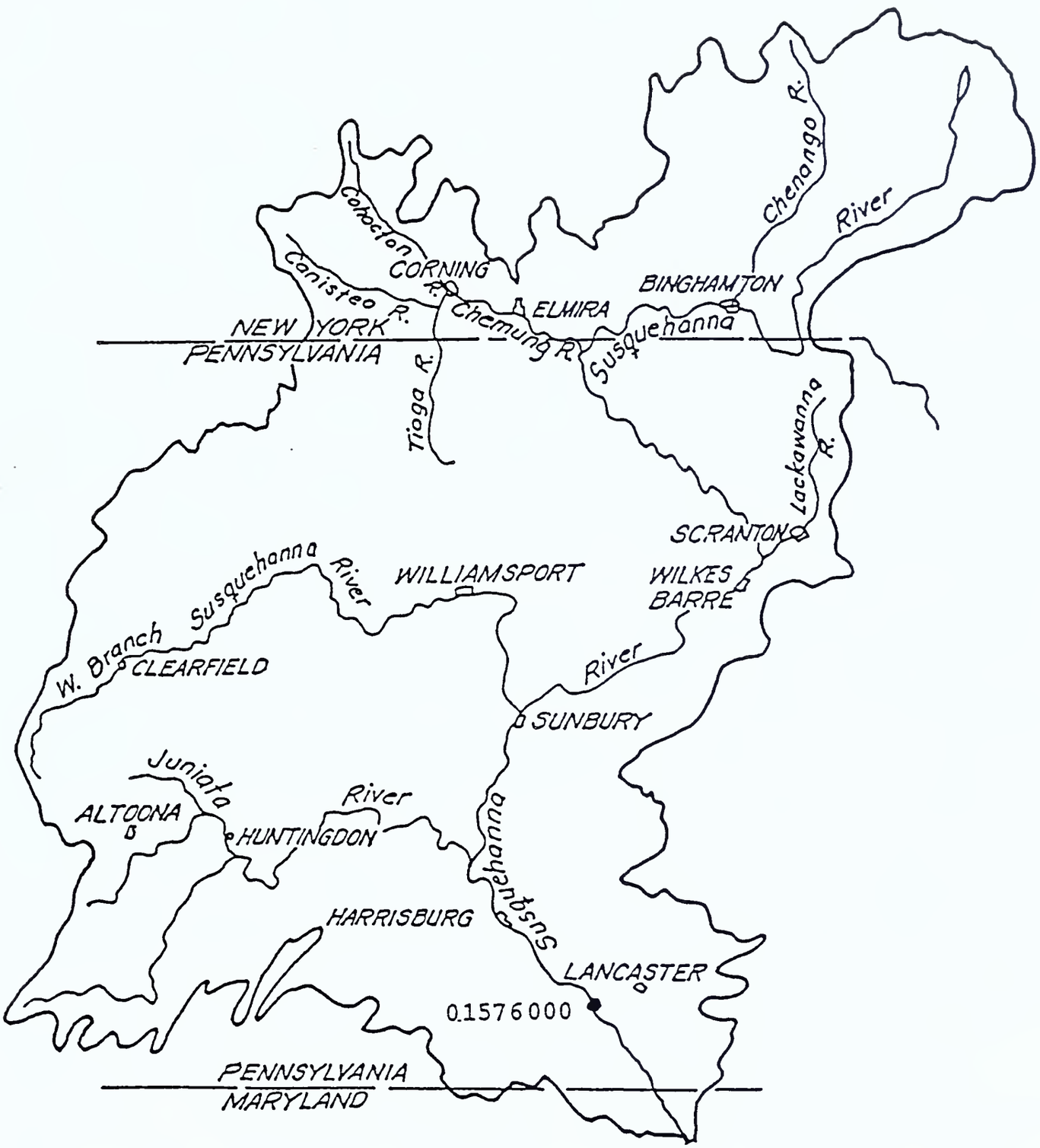

FIGURE 1.--Location of sampling site 01576000, Susquehanna River at Marietta, Pa.

the mountain and ridge land in the Juniata River and the lower Susquehanna River basins. Most of the grassland is in the northern basin. Farmers in the northern basin use more land for pasture and hay and less for cultivated crops because of the shorter and more uncertain growing season. Woods and grasslands occupy areas in the lower basin that are unsuitable for cultivation because the slopes are too steep, the soils are too stony, or the soils are poorly drained.

Most of the cultivated land is in the lower basin; however, extensive areas are cultivated along the river valleys in southern New York and along the West Branch Susquehanna River from Northumberland to Lock Haven, including the Bald Eagle Creek valley.

Major urban areas in the lower basin include York, Lancaster, Harrisburg, and Sunbury. Most of the urban areas in the northern basin are located along the river valleys. They include the Binghamton and the Elmira-Corning areas in New York, and the Scranton and Wilkes-Barre area in Pennsylvania. The major urban areas in the West Branch Susquehanna River basin are Williamsport and Lock Haven.

TOXIC MONITORING SITE

Data were collected from the Susquehanna River at Marietta, Pa. (fig. 1). This site was selected because it is the southern-most sampling site located upstream from the reservoirs in the lower Susquehanna River basin. Samples collected here would be representative of the metals and pesticides transported by its 25,990-square-mile drainage area.

SAMPLE COLLECTION AND ANALYSIS

Samples were collected at Marietta to measure concentrations of metals and pesticides listed in table 1. Base-flow samples for metals were collected monthly from May 1991 through April 1992, except in January 1992, when the river site was iced over and in April 1992 when periodic rainfall kept the river levels fluctuating throughout the month. Base-flow samples for pesticides were collected monthly from May through December 1991 and in the months of February and March 1992.

Stormflow samples were to be collected in the spring after the crops were planted and again in late summer to cover the period of most intensive pesticide application. However, samples were not collected because rainfall deficiencies, beginning in May 1991, caused drought conditions throughout basin. Storm samples were collected in late March 1992 when sufficient rain fell to cause overland runoff. Three samples were collected over the storm hydrograph; one on the rising limb, one near the peak, and one during the recession.

All samples were taken to the Pa. DER Central Lab for analysis.

TABLE 1.--Monitoring parameters, trace metals and pesticides

Trace metals	Pesticides
Arsenic, Total Recoverable	Alachlor, Total
Cadmium, Total Recoverable	Atrazine, Total
Chromium, Total Recoverable	Cyanazine, Total
Copper, Total Recoverable	Malathion, Total
Lead, Total Recoverable	Metolachlor, Total
Mercury, Total Recoverable	Prometone, Total (if possible)
Selenium, Total Recoverable	Simazine, Total
Silver, Total Recoverable	
Zinc, Total Recoverable	
Aluminum, Dissolved	
Chromium, Dissolved	
Copper, Dissolved	
Lead, Dissolved	
Nickel, Dissolved	
Zinc, Dissolved	

RESULTS

Instantaneous discharge and metals concentration data for metals are shown in table 2. Concentration shown in the table with a less-than sign (<) indicate that the constituent concentration is less than the laboratory report value. This report value has a 99 percent confidence factor that it is within 10 percent of the true value. Concentration provided in parentheses indicate an estimated concentration for which the accuracy of or confidence in the value is not known. The dash (--) indicates that the constituent concentration was below the method detection limit (MDL). The MDL has a 99 percent confidence factor that the constituent is present in the sample. The report values and method detection limits for the trace metals are shown in table 3.

TABLE 2.--Instantaneous discharge and metals concentrations, Susquehanna River at Marietta, Pa.

Date	Instant. discharge cfs	Total As	Total Se	Total Ag	Total Cd	Total Hg	Total Cr	Dis. Cr	Total Cu
					ug/l				
1991									
May 15	31,300	--	--	--	--	<0.20	--	--	4.28
Jun 20	6,830	--	--	<0.40 (0.15)	<1.00 (0.22)	<0.20	<4.00 (1.74)	<4.00 (1.66)	12.60
Jul 16	5,540	--	--	<0.40 (0.154)	4.43	<0.20	<4.00 (0.84)	<4.00 (0.84)	11.40
Aug 5	4,130	--	--	--	<1.00 (0.447)	<0.20	<4.00 (1.53)	<4.00 (1.53)	5.90
Sep 18	4,040	--	--	<0.40 (0.158)	<1.00 (0.222)	<0.20	<4.00 (0.859)	<4.00 (0.83)	6.53
Nov 20	33,800	--	--	<0.40 (0.334)	<1.00 (0.310)	<0.20	<4.00 (0.910)	<4.00 (0.910)	<4.0 (3.77)
Dec 11	27,100	--	--	<0.40 (0.310)	<1.00 (0.418)	<0.20	<4.00 (2.80)	<4.00 (1.96)	4.44
1992									
Feb 6	17,600	--	<7.50 (1.60)	--	--	<0.20	--	--	<4.00 (1.37)
Mar 18	46,800	--	--	<0.40 (0.117)	--	0.43	--	--	<4.00 (3.37)
Mar 26	31,900	--	--	--	<1.0 (0.246)	<0.20	--	--	<4.00 (2.59)
Mar 27	72,300	<4.0 (2.45)	--	--	--	<0.20	7.33	--	19.40
Mar 29	172,000	<4.0 (3.1)	--	<0.40 (0.118)	<1.00 (0.244)	<0.20	<4.00 (2.97)	--	23.40
Mar 30	146,000	<4.0 (2.44)	--	<0.40 (0.168)	<1.00 (0.418)	<0.20	4.48	--	11.10
Mar 31	120,000	--	--	<0.40 (0.129)	<1.00 (0.217)	<0.20	<4.00 1.38	--	5.44
Apr 2	92,300	--	--	--	--	<0.20	--	--	4.10
Apr 6	62,500	--	--	<0.40 (0.094)	--	<0.20	--	--	<4.00 (3.32)

< = less than report value
( ) = estimated concentration but below report value
-- = less than the method detection limit

TABLE 2.--Instantaneous discharge and metals concentrations, Susquehanna River at Marietta, Pa.--Continued

Date	Instant. discharge cfs	Dis. Cu ug/l	Total Pb ug/l	Dis. Pb ug/l	Total Ni ug/l	Dis. Ni ug/l	Total Zn ug/l	Dis. Zn ug/l	Total Al ug/l
1991									
May 15	31,300	<4.00 (2.56)	1.89	--	5.97	3.28	14.1	<5.00 (3.90)	47.5
Jun 20	6,830	6.78	2.11	<1.50 (0.470)	5.72	4.71	9.70	7.85	31.0
Jul 16	5,540	11.10	2.40	<1.50 (0.840)	4.88	4.03	24.0	18.6	57.4
Aug 5	4,130	4.72	<1.50 (1.00)	<1.50 (0.329)	4.87	4.12	12.0	6.73	35.7
Sep 18	4,040	5.59	1.83	<1.50 (0.803)	6.96	6.43	10.3	8.03	37.0
Nov 20	33,800	<4.00 (2.59)	1.73	<1.50 (0.383)	<4.00 (3.19)	<4.00 (2.70)	7.92	5.25	21.2
Dec 11	27,100	<4.00 (3.54)	1.95	<1.50 (0.461)	6.39	4.07	15.4	7.23	37.6
1992									
Feb 6	17,600	<4.00 (1.17)	<1.50 (0.305)	--	4.86	4.17	5.63	<5.0 (3.61)	16.3
Mar 18	46,800	<4.0 (1.42)	1.56	--	5.23	<4.0 3.39	15.8	6.44	20.7
Mar 26	31,900	<4.00 (1.97)	<1.50 (1.02)	--	5.23	4.23	12.7	6.09	22.8
Mar 27	72,300	10.20	15.60	<1.50 (0.357)	11.30	<4.0 (3.27)	53.5	10.30	48.3
Mar 29	172,000	15.80	12.80	<1.50 (1.37)	16.10	<4.0 (2.72)	61.5	9.45	25.1
Mar 30	146,000	<4.00 (1.57)	7.65	--	13.30	<4.0 (2.73)	51.7	5.00	33.7
Mar 31	120,000	<4.00 (2.54)	4.15	<1.50 (0.236)	8.71	<4.0 (3.37)	30.4	14.10	37.2
Apr 2	92,300	<4.00 (2.08)	1.99	--	6.02	<4.0 (2.78)	21.6	9.09	22.3
Apr 6	62,500	<4.00 (1.15)	<1.50 (1.28)	--	7.04	4.18	23.5	8.30	23.5

< = less than report value
( ) = estimated concentration but below report value
-- = less than the method detection limit

TABLE 3.--Method detection limits (MDL) and report values for trace metals analysis

Trace metals	MDL	Report value
	ug/l	
Arsenic, Total Recoverable	1.8	4.0
Cadmium, Total Recoverable	0.20	1.0
Chromium, Total Recoverable	0.80	4.0
Copper, Total Recoverable	0.80	4.0
Lead, Total Recoverable	0.20	1.5
Mercury, Total Recoverable	0.20	0.20
Nickel, Total Recoverable	0.80	4.0
Selenium, Total Recoverable	1.60	7.5
Silver, Total Recoverable	0.08	0.4
Zinc, Total Recoverable	1.0	5.0
Aluminum, Dissolved	2.0	1.0
Chromium, Dissolved	0.80	4.0
Copper, Dissolved	0.80	4.0
Lead, Dissolved	0.20	1.5
Nickel, Dissolved	0.80	4.0
Zinc, Dissolved	1.0	5.0

Copper (Cu), lead (Pb), nickel (Ni), zinc (Zn), and aluminum (Al) were the most prevalent metals transported by the Susquehanna at Marietta. Zn and Al were definitely quantified in all samples collected. Ni was definitely quantified in 15 of 16 samples; Cu in 11 of 16 samples, and Pb in 12 of 16 samples; however, they were detected in all samples. Mercury (Hg) was detected in all samples, but the concentrations were less than the report value in 15 of 16 samples. Cu, Pb, Ni, and Zn concentrations are storm related where concentrations increase with increasing flow. Hg and Al do not show any definite relationship with stormflow. The limited data do not show any seasonal variations although the storm-related metals have a higher average concentration during the winter (January to March) when stormflows were sampled.

Mercury, copper, and lead are listed in the Chesapeake Bay Toxics of Concern List (U.S. EPA, May 1991) and zinc is listed in the secondary list for future consideration for possible inclusion in the primary list. Maximum contaminant levels (MCL) for drinking water listed in the Toxics of Concern List Information Sheets (U.S. EPA, May 1991) are mercury, 2.0 ug/1; copper, none, proposed is 1,300 ug/1; and lead, 50 ug/1, proposed is 5.0 ug/1. The criteria for zinc in domestic water supplies, as listed in the Quality Criteria for Water (U.S. EPA, July 1976), is 5 mg/1. The concentrations of these metals did not exceed the drinking water criteria, but lead concentrations during the storm period exceeded the EPA proposed revision of 5.0 ug/1 lead. Copper concentrations exceeded the Pennsylvania Freshwater Acute Standard for protection of aquatic life of 18 ug/1 in two storm samples.

Silver (Ag), cadmium (Cd) and chromium (Cr) were detected in 10 of 16 samples. Concentrations of Ag were not definitely quantified. Cadmium concentration in one sample was definitely quantified; however, the value appears to be an anomaly. The reason for this is not known. Chromium concentrations were definitely quantified in two samples collected during the storm period. Cadmium and chromium are listed in the Chesapeake Bay Toxics of Concern List. The concentrations of these metals detected in the samples did not exceed the drinking water criteria of 10 ug/1 for Cd and 50 ug/1 for Cr, nor the Pennsylvania Freshwater Acute Standard for protection of aquatic life of 3.9 ug/1 for Cd and 16 ug/1 for Cr.

Arsenic (As) was detected in the three samples which were collected during stormflow, but the concentrations could only be estimated. Arsenic is listed in the secondary toxics of concern list for possible inclusion in the

primary list in the future. The criteria for arsenic in domestic water supplies is 50 ug/l, which is considerably higher than the concentrations found.

Instantaneous discharges and pesticide concentration data are shown in table 4. The pesticides listed in table 1 were selected because they were detected at Conowingo Dam, Md., by the USGS in Towson, Md. Analysis for prometone was not done because the laboratory could not develop the methodology. The method detection limits and report values for these and other pesticides detected during analysis are listed in table 5.

Atrazine was the only targeted pesticide detected. Estimated concentrations of atrazine were reported in 2 of 12 samples. Two pesticides which were not targeted were also detected. Propazine was detected in 5 of 12 samples, but only 1 sample contained propazine in definitely quantifiable concentration. Lindane was detected in 3 of 12 samples in only estimated concentrations.

Stormflows did not occur during the period of intensive pesticide use; therefore, pesticide concentrations from overland runoff during this period was not measured. Pesticides were not detected in stormflows that occurred in March 1992, possibly because runoff occurred nearly a year after pesticide application in the spring of 1991 and prior to new applications of pesticides.

Atrazine is listed in the Chesapeake Bay Toxics of Concern List. The estimated concentrations detected in the samples were less than the Adult Lifetime Health Advisory Level for Drinking Water of 3.0 ug/l listed in the

TABLE 4.--Instantaneous discharge and pesticide concentrations, Susquehanna River at Marietta, Pa.

Date	Instantaneous discharge cfs	Total Alachlor	Total Atrazine	Total Cyanazine	Total Malathion	Total Prometone
			ug/l			
1991						
May 15	31,300	--	<0.32 (0.19	--	--	--
Jun 20	6,830	--	--	--	--	--
Jul 16	5,540	--	--	--	--	--
Sep 4	3,689	--	--	--	--	--
Sep 18	4,040	--	--	--	--	--
Oct 9	3,770	--	--	--	--	--
Nov 20	33,800	--	<0.32 (0.182)	--	--	--
Dec 26	27,100	--	--	--	--	--
1992						
Feb 6	17,600	--	--	--	--	--
Mar 27	72,300	--	--	--	--	--
Mar 29	172,000	--	--	--	--	--
Mar 31	120,000	--	--	--	--	--

< = less than report value
( ) = estimated concentration but below report value
-- = not detected

TABLE 4.--Instantaneous discharge and pesticide concentrations, Susquehanna River at Marietta, Pa.--Continued

Date	Instantaneous discharge cfs	Total Simazine ug/l	Total Propazine ug/l	Total Lindane ug/l	Total Metolachlor ug/l
1991					
May 15	31,300	--	--	--	--
Jun 20	6,830	--	--	--	--
Jul 16	5,540	--	--	--	--
Sep 4	3,689	--	<0.400 (0.379)	<0.01 (0.005)	--
Sep 18	4,040	--	--	<0.01 (0.005)	--
Oct 9	3,770	--	<0.400 (0.300)	--	--
Nov 20	33,800	--	0.400	<0.01 (0.0035)	--
Dec 26	27,100	--	<0.400 (0.275)	--	--
1992					
Feb 6	17,600	--	<0.400 (0.238)	--	--
Mar 27	72,300	--	--	--	--
Mar 29	172,000	--	--	--	--
Mar 31	120,000	--	--	--	--

< = less than report value
( ) = estimated concentration but below report value
-- = not detected

TABLE 5.--Methods detection limits (MDL) and report values for pesticides analysis

Pesticide	MDL ug/l	Report value ug/l
Alachlor, Total	0.04	0.08
Atrazine, Total	0.21	0.32
Cyanazine, Total	0.02	0.40
Malathion, Total	0.10	0.20
Prometone, Total (if possible)		
Simazine, Total	0.21	0.32
Propazine, Total	0.35	0.40
Lindane, Total	0.005	0.01
Metolachlor, Total	0.10	0.20

Chesapeake Bay Toxics of Concern List Information Sheet. Alachlor and metolachlor are listed in the secondary list for possible inclusion in the primary list in the future; however, these pesticides were not detected during the sampling period.

SUMMARY

Data collected during the one-year sampling program were very limited because rainfall deficiencies caused drought conditions for most of the year. Seasonal variation and differences is base-flow and stormflow concentrations of metals and pesticides could not be evaluated.

Copper, lead, nickel, zinc, and aluminum were the most prevalent metals transported by the Susquehanna River at Marietta. The concentrations of these metals were definitely quantified in all samples. Based on data collected from one storm, copper, lead, nickel, and zinc concentrations are storm related because concentrations increase with increased flow. Copper and lead are listed in the Chesapeake Bay Toxics of Concern List and zinc is listed in the secondary list for consideration for inclusion in the primary list.

Mercury was detected in all samples, but the concentration was definitely quantifiable in only one sample. Concentrations for all other samples were less than the laboratory report value. Mercury is also listed in the Toxics of Concern List.

Silver, cadmium, and chromium were detected in 10 of 16 samples with nearly all concentrations below the report value. Chromium concentrations appear to be storm related because the concentration exceeded the report value

in the storm samples only. Cadmium and chromium are included in the Toxics of Concern List.

Arsenic was detected in concentrations less than the laboratory report value only in the three stormflow samples, which suggests that arsenic transport may be storm related. It is also included in the secondary Toxics of Concern List.

Atrazine was the only pesticide detected out of the seven that were originally selected for monitoring. Atrazine was detected in concentrations that were less than the laboratory report value in 2 of 12 samples. Atrazine is on the Toxics of Concern List.

Propazine and lindane, which were not on the parameter list, were also detected. Propazine was detected in 4 of 12 samples in concentrations at or below the laboratory report value. Lindane was detected in 3 of 12 samples collected.

Pesticides were not detected in samples collected during the single stormflow event that occurred in March 1992, possibly because runoff occurred nearly a year after pesticide application and prior to new pesticide application. Stormflows did not occur during the period of intensive pesticide use.

RECOMMENDATION

Continued monitoring for trace metals, particularly those on the Toxics of Concern Lists, and for pesticides including propazine and lindane is

recommended. The pesticide list should be expanded to include those on the Toxics of Concern Lists and those that are commonly being used in Pennsylvania. Pesticide monitoring should emphasize sample collection during periods of intensive use with periodic sampling during the non-growing season to monitor residual pesticides.

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SUSQUEHANNA RIVER BASIN COMMISSION
DEC. 24, 1970
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